Thermodynamic approach for Lyapunov based control

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Abstract: This paper focuses on non linear control of non isothermal Continuous Stirred
Tank Reactors (CSTRs). The model of the CSTR is thermodynamically consistent in order
to apply the control strategy based on the concavity of the entropy function and the use of
thermodynamic availability as Lyapunov function. More precisely the stabilization problem of
continuous chemical reactors is addressed operated at an unstable open loop equilibrium point.
The chosen control variable is the jacket temperature. In this paper we propose a state feedback
strategy to insure asymptotic stability with physically admissible control variable solicitations.
Theoretical developments are illustrated on a first order chemical reaction.

Keywords: Lyapunov based control, Irreversible thermodynamics, Non isothermal CSTR,
Multiple steady states, Entropy.

1. INTRODUCTION

Continuous Stirred Tank Reactors (CSTR) have been
widely studied in the literature with respect to process con-
trol design (Luyben (1990); Alvarez (1999); Hua (2000);
Guo (2001); Hoang (2008)). Numerous strategies have
been developed to control such non linear systems. Let
us cite for example: feedback linearization (Viel (1997))
for control under constraints, nonlinear PI control (Al-
varez (1999)), classical Lyapunov based control (Antonel-
lia (2003)), nonlinear adaptive control (Guo (2001)) and
more recently thermodynamical Lyapunov based control
(Hoang (2008)).

Besides these control problems, observation/estimation
strategies have been developed in the case of under sen-
sored CSTRs (Gibon-Fargeot (2000); Dochain (2009)).
Usually, the reactor temperature is the only on-line avail-
able measurement. Then the purpose is to estimate the
missing state variables that are used in the control strat-
egy.

In this paper we focus on the control purposes only and
we assume that concentrations and temperature are mea-
sured. This control synthesis is based on thermodynamic
concepts defined in Callen (1985) and more recently in
(Ruszkowski (2005); Ydstie (1997)) and (Hoang (2008)).
More precisely, we propose a Lyapunov based approach for
the stabilization of CSTR about unstable steady state as
in (Hoang (2008)). This is done thanks to the Lyapunov
function issued from thermodynamics consideration: the
availability function $\mathcal{A}$ (Ruszkowski (2005)).

In Hoang (2008), we proposed feedback laws involving
inlet and jacket temperatures as well as inlet flows. These
feedback laws were obtained by imposing that the time
derivative of the availability $\mathcal{A}$ remains negative, insuring
consequently the global asymptotic stability. However, no
care was given on the amplitude of the controls. Moreover
the temperature of the reactor had to be inverted and the
feedback laws had in some case some oscillatory behaviors
about the critical point.

The main contribution of this paper with respect to previ-
ous work (Hoang (2008)) is the redesign of the exponential
asymptotic controller in order to prevent excessive control
demand and oscillation problems. In this way the obtained
controller is practically more efficient. The price to pay
is that global asymptotic stability is obtained on some
validity domain only.

This paper is organized as follows: in section 2, we remind
thermodynamical concepts and variables necessary to con-
struct thermodynamic availability. This latter function is
the Lyapunov candidate of the method. In section 3 the
dynamic model of the considered CSTR is presented and
analyzed. Section 4 is devoted to the design of the state
feedback insuring asymptotic stability. Simulation results
are given in section 5. It is shown that the resulting control
leads to admissible manipulated control variables.

2. THERMODYNAMIC BASIS FOR AN AVAILABILITY FUNCTION

Irreversible thermodynamics concept will play a leading
role in the methodology used for the design of the Lya-
punov function (Ruszkowski (2005); Hoang (2008)). In
this section we review the main ideas concerning this
thermodynamical approach and the construction of the
candidate Lyapunov function: the availability function in
the case of an homogeneous phase.

In equilibrium thermodynamics, the system variables are divided into extensive and intensive variables, depending on whether their values depend on the "size" of the system or not. The internal energy of a homogeneous system is then expressed in terms of products of pairings of energy conjugate variables such as pressure P/ volume V, temperature T/ entropy S and chemical potential μ_i/ mole number n_i for each species i of the mixture.

The fundamental relation of thermodynamics expresses the entropy S of a given phase as a function of the so called extensive variables $Z = (U, V, n_i)$ by the Gibbs equation:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV + \sum_{i=1}^{n_c} \frac{-\mu_i}{T}dn_i. \qquad (1)$$

It can also be written as:

$$dS = w^T dZ \qquad (2)$$

with $w = (\frac{1}{T}, \frac{P}{T}, \frac{-\mu_i}{T})$.

Since the entropy S is an extensive variable, it is a homogenous function of degree 1 of Z (Callen (1985)). From Euler's theorem we get:

$$S(Z) = w^T Z \qquad (3)$$

Equation (2) can also be applied in irreversible thermodynamics as soon as the local state equilibrium is assumed: it postulates that the present state of the homogeneous system in any evolution can be characterized by the same variables as at equilibrium and is independent on the rate of evolution. So (2) can also be applied at any time.

Moreover, it is well known that balance equations can be established for $Z = (U, V, n_i)$ as well as for the entropy S but this latter is not conservative: in irreversible thermodynamics there is a source term σ which is always positive from the the second law of thermodynamics. This term represents the irreversible entropy production: the energy $T\sigma$ associated to this term represents the energy lost from material, space or thermal domains and that will never more contribute to some physical works. As a consequence of (2), the entropy balance can alternatively be written as:

$$\frac{dS}{dt} = w^T \frac{dZ}{dt} \qquad (4)$$

Finally let us notice that for homogeneous thermodynamical systems (one phase only), the entropy function $S(Z)$ is necessarily strictly concave (see Callen (1985)) as shown in Fig. 1.
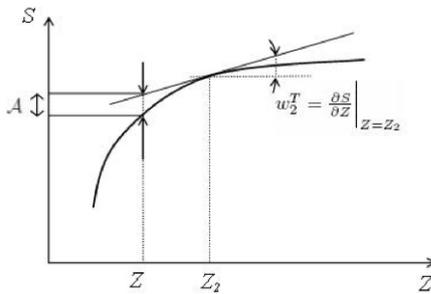

Fig. 1. Entropy and availability functions w. r. to Z.

From these observations, it can be shown (see Ydstie (1997)) that the non negative function:

$$\mathcal{A}(Z) = S_2 + w_2^T(Z - Z_2) - S(Z) \geq 0 \qquad (5)$$

where Z_2 is some fixed reference point (for example the desired set point for control), is a measure of the distance between entropy $S(Z)$ and its tangent plane passing through Z_2. It is geometrically presented in Fig. 1. The slope of the tangent plane is related to intensive vector $w(Z)$ calculated at $Z = Z_2$.

As soon as we consider homogeneous mixture, S remains concave and then $\mathcal{A}$ remains also non negative. As a consequence, A is a natural Lyapunov candidate. It remains to build a feedback law to insure:

$$\frac{d\mathcal{A}}{dt} \leq 0. \qquad (6)$$

3. CASE STUDY: A NON ISOTHERMAL CSTR MODEL

3.1 Assumptions of the model

We consider a jacketed homogeneous CSTR with the following first-order chemical reaction: $A \rightarrow B$. The temperature of the jacket T_w is supposed to be uniform and is used for the control purpose. The dynamics of the CSTR is deduced from volume, material and energy balances.

The following assumptions are made:

- The fluid is incompressible and the reaction mixture is supposed to be ideal.
- The two species are supposed to have the same partial molar volume v.
- At the inlet of the reactor, the pure component A is fed at temperature T_e.
- The reaction volume V is supposed to be constant.
- The heat flow exchanged with the jacket is represented by $\dot{Q} = \lambda(T_w - T)$.
- The kinetics of the liquid phase reaction is modelled thanks to the Arrhenius law. The reaction rate r_v is given by $k_0 \exp(\frac{-k_1}{T})\frac{n_A}{V}$.

In Tables (1,2) are given the notations and numerical values that will be used for modelling and simulation. Finally let us notice that constant volume assumption

Notation	unit	
F_{Ae}	mol/s	Inlet molar flow rate of A
F_A	mol/s	Outlet molar flow rate of A
F_B	mol/s	Outlet molar flow rate of B
F	mol/s	Total outlet molar flow rate
h_{Ae}	J/mol	Inlet molar enthalpy of A
h_i	J/mol	Molar enthalpy of species i $(i = A, B)$
H	J	Total enthalpy of the mixture
n_A	mol	Mole number of species A
n_B	mol	Mole number of species B
T	K	Temperature in the CSTR
n_T	mol	Total mole number
r_v	$mol/m^3/s$	Reaction rate
U	J	Internal energy
$x_i = \frac{n_i}{n_T}$		Molar fraction of species i, $i = A, B$

Table 1. Notation of the variables of the model.

implies that the total number of moles n_T is constant since the two species have the same partial molar volume.

	Numerical value	
C_{pA}	75.24 $(J/K/mol)$	Heat capacity of species A
C_{pB}	60 $(J/K/mol)$	Heat capacity of species B
h_{Aref}	0 (J/mol)	Reference enthalpy of A
h_{Bref}	-4575 (J/mol)	Reference enthalpy of B
k_0	0.12 10^{10} $(1/s)$	Kinetics constant
k_1	8.7 10^3 (K)	Parameter in Arrhenius law
P	10^5 (Pa)	Pressure
T_{ref}	300 (K)	Reference temperature
v	0.0005 (m^3/mol)	Molar volume
V	0.001 (m^3)	Reaction volume
λ	0.05808 (W/K)	Heat transfer coefficient
s_{Aref}	210.4 $(J/K/mol)$	Reference entropy of A
s_{Bref}	180.2 $(J/K/mol)$	Reference entropy of B

Table 2. Parameters of the CSTR.

Moreover the constant volume assumption constrains the total outlet molar flow rate F.

3.2 CSTR modelling

The material balances are given by:

$$
\begin{cases}
\dfrac{dn_A}{dt} = F_{Ae} - F_A - r_{\mathrm{v}}V \\
\dfrac{dn_B}{dt} = -F_B + r_{\mathrm{v}}V
\end{cases}
\tag{7}
$$

and the energy balance by:

$$
\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} + F_{Ae}h_{Ae} - (F_A h_A + F_B h_B) \tag{8}
$$

Remark 1. Since we suppose ideality of the mixture, the enthalpy of species A_i, $i = A, B$ in the mixture can be expressed as: $h_i(T) = c_{pAi}(T - T_{ref}) + h_{iref}$. Let us furthermore note that, as the species are involved in a chemical reaction, the reference molar enthalpies are chosen with regard to the enthalpy of formation of species.

Finally the volume balance leads to:

$$
\frac{dV}{dt} = 0 \tag{9}
$$

Since molar volume of species are assumed to be equal, it implies that $F = F_{Ae}$ and $F_A = x_A\, F_{Ae}$ and $F_B = x_B\, F_{Ae}$

The internal energy balance can be written in term of temperature. This is done by using the expression of the enthalpy of the system $H = \sum_{i=A,B} n_i h_i$ and by noticing that under our assumptions $\frac{dU}{dt} = \frac{dH}{dt}$. We finally obtain:

$$
C_p \frac{dT}{dt} = \left(-\Delta H\right)r_{\mathrm{v}}V + F_{Ae}C_{pA}(T_e - T) + \lambda(T_w - T) \tag{10}
$$

where $\Delta H = (h_B - h_A)$ is the enthalpy of the reaction and $C_p = C_{pA}n_A + C_{pB}n_B$ is the total heat capacity.

The dynamics of states variables (H, n_A) ((8) and (7)) or (T, n_A) ((10) and (7)) give two equivalent representations of the CSTR. These representations will be used for late purpose.

3.3 Analysis of the steady states

For this purpose, manipulated variables are chosen as:

$$
F_{Ae} = 0.0183\ (mol/s),\ T_e = 310\ (K)\ T_w = 300\ (K) \tag{11}
$$

Steady states are calculated by setting (7) and (10) equal to zero.

By introducing the expression of the steady state mole number of n_A in the temperature equation, the steady state temperatures are the values that satisfy $P_e(T) = 0$ with:

$$
\begin{aligned}
P_e(T) = {} & \frac{h_A - h_B}{C_p}k_0 \exp\left(\frac{-k_1}{T}\right)\frac{F_{Ae}}{\left(\frac{F_{Ae}}{n_T} + k_0 \exp\left(\frac{-k_1}{T}\right)\right)} \\
& + \frac{F_{Ae}C_{pA}}{C_p}(T_e - T) + \frac{\lambda}{C_p}(T_w - T)
\end{aligned}
\tag{12}
$$

These values are represented in Fig. 2(a). It shows that the system has three steady state operating points: P_1, P_2 and P_3.
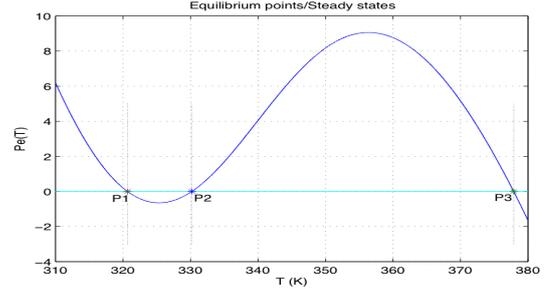

Fig. 2. Steady states

The numerical values of these steady states and the eigenvalues of the linearized system about these points are given in Table 3.

Points	Values	Eigenvalues
P_1: $[n_A\ T]$	[1.6449 320.6704]	[$-0.0090\ -0.0024$]
P_2: $[n_A\ T]$	[1.3583 330.1997]	[$-0.0090\ 0.0027$]
P_3: $[n_A\ T]$	[0.1416 377.8795]	[$-0.0802\ -0.0100$]

Table 3. Steady state points and eigenvalues

From Table 3, one can see that steady state operating points P_1 and P_3 are stable, whereas the steady state operating point P_2 is not stable since one of its eigenvalues is positive.

Control Problem: we are interested to operate the reactor at $T = 330.1997$ corresponding to the unstable steady state operating point P_2 and at fixed F_{Ae} and T_e. As a consequence a control feedback law on T_w is necessary.

4. CONTROLLER SYNTHESIS

In this paper we propose a feedback law that is less conservative than the one proposed in Hoang (2008) and that still insures asymptotic stability in some admissible domain. We first give some preliminary results necessary for the controller synthesis.

Proposition 1 shows that n_A belongs to an invariant domain $[0, n_T]$.

Proposition 1. If $n_A(0) \in [0, n_T]$ then $n_A(t) \in [0, n_T]$ $\forall t$

Proof. It is straightforward looking at (7) since $\left.\frac{dn_A}{dt}\right|_{n_A=0} = F_{Ae} > 0$ and $\left.\frac{dn_A}{dt}\right|_{n_A=n_T} = -k_0\exp(-\frac{k_1}{T})n_T < 0$ $\qquad \square$

Moreover we notice that the sign of $\frac{dn_A}{dt}$ is the same as that of $G(T) = \frac{F_{Ae}}{\frac{F_{Ae}}{n_T} + k_0 \exp(\frac{-k_1}{T})}$.

In order to stabilize the closed loop system about (n_{a_2}, T_2), we propose the following feedback law for T_w.

Proposition 2. At fixed T_e and F_{Ae}, the system defined by ((7) and (8)) with the non linear feedback law (13) for T_w:

$$T_w = \frac{1}{\lambda}\left(K_1\widetilde{v}_1 - \mathfrak{F}F_{Ae} + \frac{f}{-\widetilde{v}_1}\frac{dn_A}{dt}\right) + T \qquad (13)$$

where:

$$\widetilde{v}_1 = \left[\frac{1}{T} - \frac{1}{T_2}\right] \qquad (14)$$

$$\mathfrak{F}(T_e, T, n_A, n_B) = \left(h_{Ae} - (x_A h_A + x_B h_B)\right) \qquad (15)$$

and

$$f(T) = \left((C_{pA} - C_{pB})T_{ref} - (h_{Aref} - h_{Bref})\right)\widetilde{v}_1 \\ + \left(C_{pA} - C_{pB}\right)\ln\left(\frac{T}{T_2}\right) \qquad (16)$$

is stable and asymptotically converges to the desired operating point $P_2 = (T_2, n_{A2})$ for any initial condition (T_0, n_{A0}) contained in some validity domain for which the constant K_1 is chosen positive.

Proof. K_1 insures the continuity of T_w at $t = 0$: $T_w(0) = T_0$ or,

$$\left[K_1\widetilde{v}_1 - \mathfrak{F}F_{Ae} + \frac{f}{-\widetilde{v}_1}\frac{dn_A}{dt}\right]_{t=0} = 0 \qquad (17)$$

The proof of the proposition 2 contains two parts:
1. Determination of the validity domain of initial conditions: developing (17) and using the material balance (7) and since $n_B = n_T - n_A$, we have at $t = 0$:

$$K_1\widetilde{v}_1 = F_{Ae}h_{Ae} - F_{Ae}h_B + \frac{f}{\widetilde{v}_1}F_{Ae} - n_A D(T) \qquad (18)$$

with $D(T) = \left[\frac{F_{Ae}}{n_T}(h_A - h_B) + \left(\frac{F_{Ae}}{n_T}F_{Ae} + k_0\exp(\frac{-k_1}{T})\right)\frac{f}{v_1}\right]$. For positive K_1, (18) is positive if $\widetilde{v}_1 > 0$. So the right hand side of the equality has the sign of $\widetilde{v}_1$.

In a same way, we obtain :

$$\begin{cases} n_{A0} < F(T_0) \text{ if } T_0 > T_2 \\ n_{A0} > F(T_0) \text{ if } T_0 < T_2 \end{cases} \qquad (19)$$

with $F(T) = \frac{(h_{Ae} - h_B + \frac{f}{v_1})}{\frac{1}{n_T}(h_A - h_B) + \frac{1}{G(T)}\frac{f}{v_1}}$.
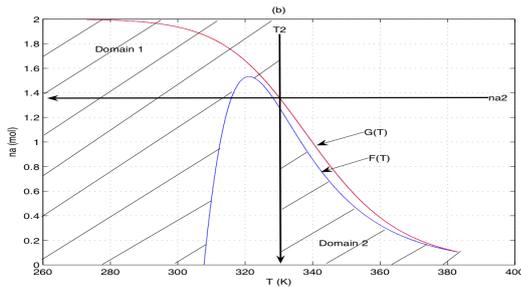
The domain of validity is given in Fig. 3.

Fig. 3. Domain of validity of initial conditions

2. Stability and convergence to the desired point (T_2, n_{A2}): Let us consider the function $\mathcal{A}$ (5). The time derivative of such function can be written:

$$\frac{d\mathcal{A}}{dt} = -\widetilde{v}_1\frac{dU}{dt} - \widetilde{v}_2\frac{dn_A}{dt} \qquad (20)$$

with $\widetilde{v}_2 = -\left(\frac{\mu_A}{T} - \frac{\mu_B}{T}\right) + \left(\frac{\mu_{A2}}{T_2} - \frac{\mu_{B2}}{T_2}\right)$. From the energy balance (8), (20) can be written:

$$\frac{d\mathcal{A}}{dt} = -\widetilde{v}_1\left[F_{Ae}\mathfrak{F} + \lambda(T_w - T)\right] - \widetilde{v}_2\frac{dn_A}{dt} \qquad (21)$$

where $\mathfrak{F}$ is defined in (14). Furthermore, using the constitutive equation

$$\mu_A(T, P, x_A) = \mu_A^0(T) + RT\ln(\frac{n_A}{n_A + n_B}) \qquad (22)$$

where $\mu_A^0(T) = C_{pA}(T - T_{ref}) + h_{Aref} - T\left(C_{pA}ln(\frac{T}{T_{ref}}) + s_{Aref}\right)$ one can write $\widetilde{v}_2$ on the following form:

$$\widetilde{v}_2 = f(T) + g(n_A) \qquad (23)$$

where $f(T)$ is defined in (16) and $g(n_A) = R\ln\left(\frac{n_{A2}}{n_A}\frac{n_B}{n_{B2}}\right)$. Then (21) becomes :

$$\frac{d\mathcal{A}}{dt} = -\widetilde{v}_1\left[F_{Ae}\mathfrak{F} + \lambda(T_w - T)\right] - (f + g)\frac{dn_A}{dt} \qquad (24)$$

We propose the following feedback law :

$$T_w = \frac{1}{\lambda}\left(K_1\widetilde{v}_1 - \mathfrak{F}F_{Ae} + \frac{f}{-\widetilde{v}_1}\frac{dn_A}{dt}\right) + T \qquad (25)$$

for systems with initial conditions $(T_w(0) = T(0))$ such that $K_1 > 0$. Using this feedback law, $\frac{d\mathcal{A}}{dt}$ becomes:

$$\frac{d\mathcal{A}}{dt} = -K_1\widetilde{v}_1^2 - g\frac{dn_A}{dt} \qquad (26)$$

The idea is to not constrain the system by imposing $\frac{d\mathcal{A}}{dt} < 0 \ \forall t$ as in Hoang (2008).

We are now going to show that depending on the initial conditions from the domain of validity (associated with condition $K_1 > 0$), $-g\frac{dn_A}{dt}$ is either negative $\forall t$ or becomes negative and converges to 0.
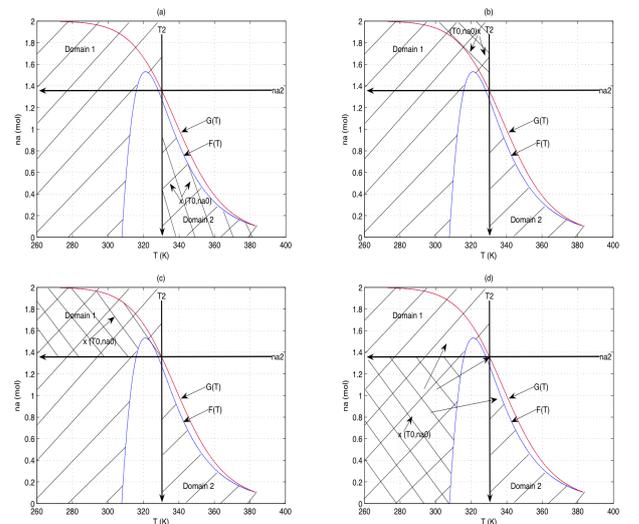

Fig. 4. Admissible initial conditions in the domain of validity.

Remark 2. A simple analysis permits to conclude that $g(n_A)$ is positive as soon as $n_A \leq n_{A2}$.

In all cases in using (19), lemma 1 and remark 2 we will show the negativeness of $-g\frac{dn_A}{dt}$.

With initial conditions such as shown in Fig. 4(a) and using additionally the remarks 4.5 and 4.6 of appendix A), we have:

$$\frac{d\mathcal{A}}{dt} = -K_1\widetilde{v}_1^2 - g\frac{dn_A}{dt} \leq 0, \ \forall t \qquad (27)$$

With initial conditions such as shown in Fig. 4(b), using the remarks 4.3 and 4.4 we obtain the same inequality (27).

The trajectory of (T, n_A) issued from initial domain as shown in Fig. 4(c) is trapped in the domain of Fig. 4(b). This is obtained thanks to remarks 4.2 and 4.3 and 4.4.

Finally for initial conditions as shown in Fig. 4(d), there are two possible scenarios : one is that the trajectory of (T, n_A) is trapped in the domain of figure 4(a) or 4(c) then 4(b). The result then follows from remarks 4.2 and 4.3 and 4.4. The other scenario is that the trajectory of (T, n_A) is not trapped in these domains and then $\mathcal{A}$ always decreases and converges to 0.

Finally, from all the admissible initial conditions and after some time, $\mathcal{A}$ plays the role of a Lyapunov function.

Remark 3. The feedback law T_w (13) is well defined for $T = T_2$ since $\lim_{T \to T_2} \frac{f}{v_1} = \left((C_{pA} - C_{pB})T_{ref} - (h_{Aref} - h_{Bref})\right) + \left(C_{pA} - C_{pB}\right)(-T_2)$.

5. SIMULATION

The purpose of this section is to illustrate the good performances obtained from the aforementionned control strategy and the admissibility of the resulting control variables. The open and closed loop simulations are carried out respect to four different initial conditions chosen in the initial domain of validity of the control law. These initial conditions correspond to the four different scenarios depicted in Fig. 4 in view of studying the convergence properties of the control law and the control variable solicitation. The four initial conditions are:

(C1): $(T(0) = 340, n_{A0} = 0.6)$ belongs to Fig. 4(a).
(C2): $(T(0) = 325, n_{A0} = 1.8)$ belongs to Fig. 4(b).
(C3): $(T(0) = 300, n_{A0} = 1.6)$ belongs to Fig. 4(c).
(C4): $(T(0) = 300, n_{A0} = 0.6)$ belongs to Fig. 4(d).

5.1 Open loop simulation

First of all let us consider open loop simulations with inputs defined by (11) and initial conditions (C1) to (C4). Simulations are given in Figure (5).
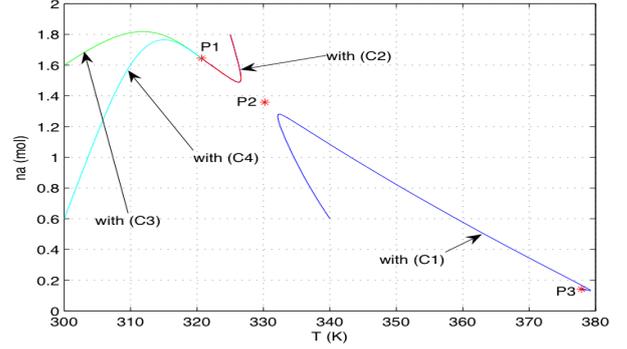

Fig. 5. The representation of the open loop phase plan

5.2 Closed loop system

The open loop system is closed with the feedback law T_w constructed with the state variables n_A and T.

The trajectories issued from the initial points (C1) to (C4) are given in Fig. 6. We notice that for all the initial conditions the system converges to the desired operating point P2.
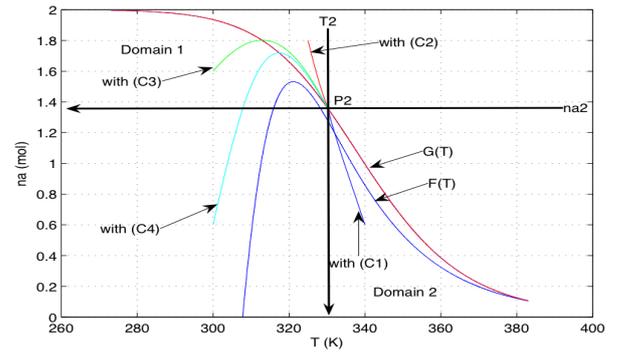

Fig. 6. Closed loop trajectories in phase plane.

Fig. 7 shows the control variable T_w. Its values are admissible and its evolution is slow enough.
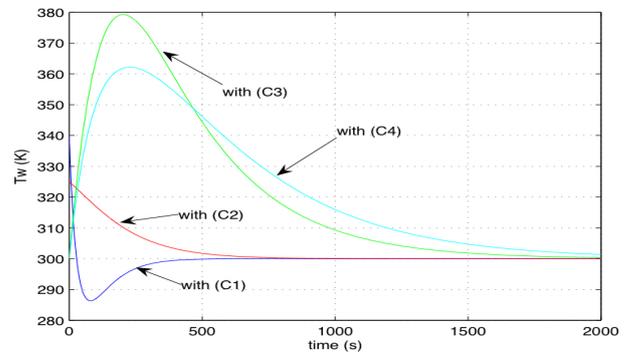

Fig. 7. The feedback law T_w

Fig.8 shows the time trajectory of $\mathcal{A}$ for the different initial conditions. For initial conditions (C1) and (C2),

the availability $\mathcal{A}$ can be assimilated to Lyapunov function from the beginning of the reaction. For initial conditions (C3) and (C4), $\frac{d\mathcal{A}}{dt}$ is forced to be negative only after a certain time from which $\mathcal{A}$ plays the role of Lyapunov function, and converges to 0.
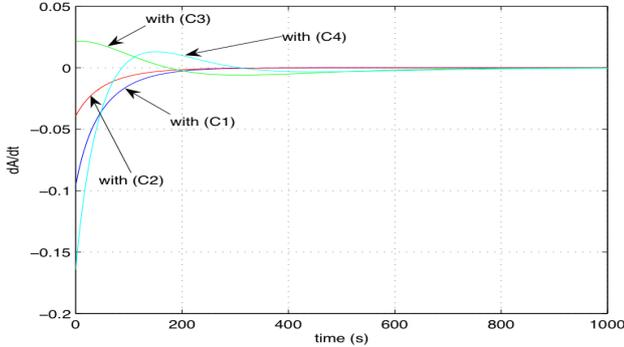

Fig. 8. The dynamics of $\frac{d\mathcal{A}}{dt}$

6. CONCLUSION

In this paper, we have shown how to stabilize a CSTR about the desired operating point by means of Lyapunov-based method. The Lyapunov function is the availability function $\mathcal{A}$. $\mathcal{A}$ is derived from thermodynamic considerations. The stabilization is ensured in some domain of validity issued from the condition of positivity of the design parameter K_1 and the continuity of the feedback law T_w.

The simulation results showed that convergence objective is satisfied and that the state feedback law is physically implementable since jacket temperature remains in some physical domain with admissible rate of variation.

Nevertheless, in the proposed control strategy the closed loop dynamic is imposed by the initial conditions (with K_1). This is the reason why we are now studying for dynamic controllers with additional freedom degrees. It remains also to compare our result with previous results as given in Viel (1997) for example) in term of performance and robustness.

REFERENCES

Alvarez-Ramirez, J. and Femat, R. (1999). Robust PI stabilization of a class of chemical reactors. *Systems & Control Letters*, 38(4-5), 219-225.

Antonellia, R., and Astolfi, A. (2003). Continuous stirred tank reactors: easy to stabilise? *Automatica*, 39, 1817-1827.

Callen, H.B. (1985). *Thermodynamics and an introduction to thermostatics.* John Wiley & Sons Inc, New York, 2nd edition.

Dochain, D., Couenne, F., and Jallut, C. (2009) Enthalpy Based Modelling and Design of Asymptotic Observers for Chemical Reactors. *accepted to International Journal of Control.*

Gibon-Fargeot, A.M., Celle-Couenne, F. , and Hammouri, H. (2000). Cascade estimation design for cstr models. *Computers & Chemical Engineering*, 24(11), 2355-2366.

Guo, B., Jiang, A., Hua, X., and Jutan, A. (2001). Nonlinear adaptive control for multivariable chemical processes. *Chemical Engineering Science*, 56, 67816791.

Hoang, H., Couenne, F.,Jallut, C., and Le Gorrec, Y. (2008). Lyapunov based control for non isothermal continuous stirred tank reactor. *Proceedings of the 17th World Congress of the IFAC*, July 6-11, 2008, Seoul, Korea.

Hua, X., and Jutan A. (2000). Nonlinear Inferential Cascade Control of Exothermic Fixed-bed Reactors. *AICHE Journal*, 46, 980-996, 2000.

Luyben, W.L. (1990). *Process Modeling, Simulation, and Control for Chemical Engineers.* McGraw-Hill, Singapore.

Ruszkowski, M., Garcia-Osorio, V., and Ydstie, B.E. (2005) Passivity based control of transport reaction systems. *AIChE Journal*, 51, 3147-3166.

Viel, F., Jadot, F., and Bastin, G. (1997). Global stabilization of exothermic chemical reactors under input constraints. *Automatica*, 33(8), 1437-1448.

Ydstie, B.E., and Alonso, A.A. (1997). Process systems and passivity via the Clausius-Planck inequality. *Systems Control Letters*, 30(5), 253-264.

Appendix A

Lemma 1. The energy balance (8) with feedback law (13) gives rise to:
1.
$$(\sum_i n_i C_{pi})\frac{dT}{dt} = K_1 \widetilde{v}_1 + L(T)\frac{dn_A}{dt} \qquad (A.1)$$

with $L(T) = \left(-\frac{f}{v_1} - (h_A - h_B) \right)$.

2. With assumptions presented in section 3.1, we have: $L(T) > 0$ if $T < T_2$ and $\lim_{T \to T_2} L(T) = 0$.

Remark 4. The following remarks hold:

(1) From Proposition 1, C_p is bounded and positive.

(2) Lemma 1 insures that if $T < T_2$ and $\frac{dn_A}{dt} > 0$ then $\frac{dT}{dt} > 0$ since $C_p \frac{dT}{dt} = K_1 \underbrace{\widetilde{v}_1}_{>0} + \underbrace{L(T)\frac{dn_A}{dt}}_{>0}$.

(3) When $\frac{dn_A}{dt} = 0$ (n_A reaches $G(T)$) and $T < T_2$ then $(\sum_i n_i C_{pi})\frac{dT}{dt} = K_1 \underbrace{\left(\frac{1}{T} - \frac{1}{T_2} \right)}_{>0}$ and $\frac{dT}{dt}$ remains positive.

(4) When $\frac{dn_A}{dt} < 0$ and $T = T_2$, then $C_p \frac{dT}{dt} = 0$ and T stays equal to T_2.

(5) When $\frac{dn_A}{dt} = 0$ (n_A reaches $G(T)$) and $T > T_2$, then $(\sum_i n_i C_{pi})\frac{dT}{dt} = K_1 \underbrace{\left(\frac{1}{T} - \frac{1}{T_2} \right)}_{<0}$ and T decreases.

(6) When $\frac{dn_A}{dt} > 0$ and $T = T_2$, then $(\sum_i n_i C_{pi})\frac{dT}{dt} = 0$ and T remains equal to T_2.

(7) When $\frac{dn_A}{dt} = 0$ and $T = T_2$, the system reaches the desired point and stays on.